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The synthesis of linear and (hyper)branched polymers possessing varying compositions using atom transfer radical polymerization (ATRP) was conducted. The synthesis of linear random and gradient copolymers from styrene/n-butyl acrylate and methyl methacrylate/n-butyl acrylate systems were evaluated by studying the copolymerization kinetics of the respective monomers pairs in ATRP. Development in the preparation of materials with advanced architectures was achieved by the synthesis of novel hyperbranched polymers using the self-condensing vinyl polymerization (SCVP) by ATRP. Subsequent end-group transformation reactions of these hyperbranched polymers yielded low viscosity materials with reactive functionalities. Additionally, novel highly branched nanocomposites were also prepared by the use of a functional colloid (diameter = 15 nm) as a macroinitiator for the synthesis of homo- and block copolymers tethered to a particle surface.

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1. Arehart, S. V.; Matyjaszewski, K. "Atom Transfer Radical Copolymerization of Styrene and n-Butyl Acrylate," Macromolecules, 1999, 32, 2221

Coessens, V.; Pyun, J.; Miller, P.J.; Gaynor, S.G.; Matyjaszewski, K. Macromolecular Rapid Commun., 2000, 21, 103-109

Ziegler, M.J.; Matyjaszewski, K. "Gradient Copolymers by Atom Transfer Radical Copolymerization," J. Phys. Org. Chem., in press

2. Scientific Personnel: One graduate student (Jeffrey Pyun taking over project from Stephen V. Arehart, in Department of Chemistry at Carnegie Mellon University)

3. Report of Inventions: No patents have been filed from research conducted under the provided grant.

4. Honors and Awards:
   K. Matyjaszewski received the A. von Humboldt prize for Senior U.S. Scientist (1999

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Final Progress Report on "Synthesis and Characterization of Gradient Hyperbranched Copolymers by Atom Transfer Radical Polymerization"

Jeffrey Pyun, Stephen V. Arehart, and Krzysztof Matyjaszewski

Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213

Statement of Problem

The synthesis of functional (hyper)branched copolymers using atom transfer radical polymerization (ATRP) was the target of the proposed research. Previously, the ability to prepare well-defined linear copolymers, or (hyper)branched homopolymers by ATRP was demonstrated. However, combination of these structural parameters into a singular material was not done previously, and was the subject of our efforts.

Accomplishments

- Determination of reactivity ratios of styrene/*n*-butyl acrylate and methyl methacrylate/*n*-butyl acrylate monomer pairs in atom transfer radical copolymerizations to ascertain tendencies toward gradient copolymer formation.
- Synthesis of novel hyperbranched polyacrylates, with the ability to transform terminal end-groups to reactive functional groups (i.e., epoxy) via radical addition processes.
- Synthesis of well-defined, highly branched nanocomposites, where the a shell of the material comprised of well-defined copolymer chains tethered to a silicate nanoparticle core.

List of Manuscripts

Arehart, S. V.; Matyjaszewski, K. "Atom Transfer Radical Copolymerization of Styrene and *n*-Butyl Acrylate," *Macromolecules*, **1999**, *32*, 2221

Coessens, V.; Pyun, J.; Miller, P.J.; Gaynor, S.G.; Matyjaszewski, K. *Macromolecular Rapid Commun.*, **2000**, *21*, 103-109

Arehart, S. V.; Matyjaszewski, K. "Gradient Copolymers by Atom Transfer Radical Copolymerization," *Macromolecules*, submitted

Scientific Personnel One graduate student (Jeffrey Pyun taking over project from Stephen V. Arehart, in Department of Chemistry at Carnegie Mellon University)

Report of Inventions No patents have been filed from research conducted under the provided grant.

Abstract: The synthesis of linear and (hyper)branched polymers possessing varying compositions using atom transfer radical polymerization (ATRP) was conducted. The synthesis of linear random and gradient copolymers from styrene/*n*-butyl acrylate and methyl methacrylate/*n*-butyl acrylate systems were evaluated by studying the copolymerization kinetics of the respective monomers pairs in ATRP. Development in the preparation of materials with advanced architectures was achieved by the synthesis of novel hyperbranched polymers using the self-condensing vinyl polymerization (SCVP) by ATRP. Subsequent end-group transformation reactions of these hyperbranched polymers yielded low viscosity materials with reactive functionalities. Additionally, novel highly branched nanocomposites were also prepared by the use of a functional colloid (diameter = 15 nm) as a macroinitiator for the synthesis of homo- and block copolymers tethered to a particle surface.

Scientific Progress and Accomplishments

Introduction. ATRP has proven to be a versatile method for the synthesis of polymers with well-defined molecular weights, compositions and functionality. ATRP proceeds through a reversible activation / deactivation process catalyzed by transition metals complexed with ligands capable of stabilizing the higher oxidations state of the metal and providing a way to dissolve the catalyst in organic solvents.[1] (Scheme 1)

Initiation (k_i) occurs by reaction of a small molecule alkyl halide with the catalyst to produce a radical (k_a). This radical can add to monomer to produce a growing polymer species capable of propagation (k_p). The propagating radical can react with itself to produce a dead chain (k_t), react with monomer (k_p) and regenerate the radical, or react with the oxidized catalyst (k_d) to produce a dormant species which will not add monomer. Reactivation of the dormant species occurs by reaction of the polymeric halide with the catalyst (k_a), regenerating the radical.

An important aspect of this catalytic system is the equilibrium between active and dormant species. This equilibrium reduces the polydispersity of the polymer as the reaction proceeds by providing equal growth probabilities for all chains. This process, in combination with rates of initiation being comparable to propagation, lower polydispersities to around 1.1, much lower than in conventional radical polymerizations.

Initiation

Propagation
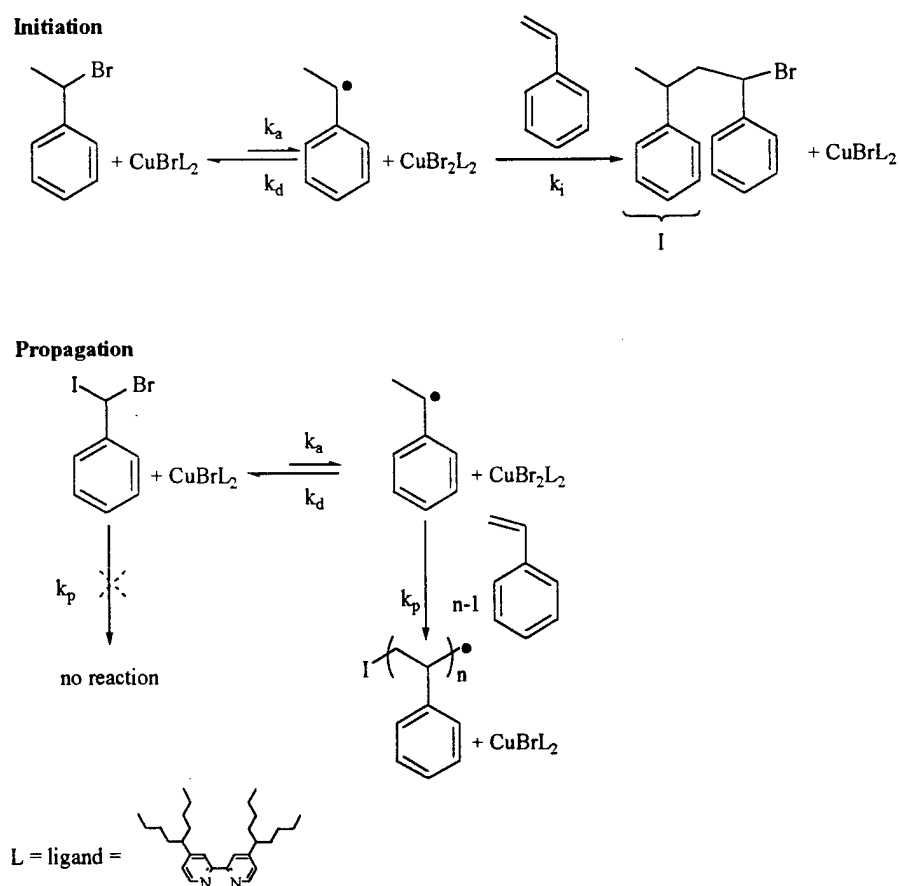
Scheme 1. Atom Transfer Radical Polymerization.

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Findings to Date One of the major requirements of any monomer pair that can potentially be used to produce hyperbranched gradient copolymers is that they must copolymerize together in a controlled manner by ATRP. In accordance with the proposed research in AASERT grant #DAA655-97-1-0191, we evaluated styrene (Sty) and *n*-butyl acrylate (BA) as potential candidates for hyperbranched copolymers since both *p*-chloromethylstyrene[2] and 2-((2-bromopropionyl)oxy)ethyl acrylate[3] can be homopolymerized by ATRP to produce hyperbranched structures. Copolymerization of styrene and *n*-butyl acrylate was evaluated in terms of kinetics, molecular weight / polydispersity behavior, and chemoselectivity.[4]

Kinetics of Copolymerization The kinetics of ATRP of styrene using CuBr/4,4'-(5-nonyl)-2,2'-bipyridine (dNBpy) as a catalyst system at 110 °C have been well-documented.[1] Under these experimental conditions, polymerizations of styrene were first order in monomer, and plots of ln ($[M]_o/[M]$) versus time were linear for several half lives of the reaction, indicating a constant concentration of active centers (no termination). Polymerizations of *n*-butyl acrylate with the same catalyst at 90 °C also show linear kinetics.

In contrast, copolymerizations of styrene and *n*-butyl acrylate do not show this linear kinetic dependence. Figure 1 plots ln $[M]_o/[M]$ versus time (s) for statistical copolymerizations of styrene and *n*-butyl acrylate for 5 different feed ratios of styrene at 110 °C. Reaction conditions for these experiments are shown in Table 1. Absolute volumes were not measured with precision in these reactions and the data in Table 1 are presented only as molar ratios in initial conditions.
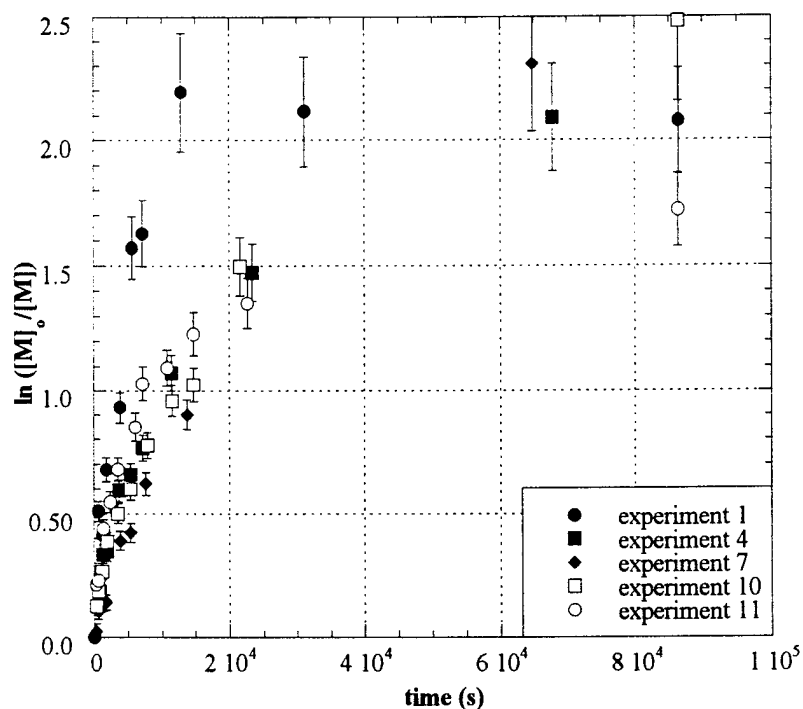
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Figure 1. Semilogarithmic kinetic plots for the simultaneous copolymerization of styrene and *n*-butyl acrylate for different initial mole fractions of styrene $(f_{st})_o$. Reaction numbers listed in the legend correspond to conditions in Table 1.

Molecular Weight and Polydispersity Behavior of Copolymerizations

Consistent with what has been reported for styrene[1] and what has been found in our laboratories for *n*-butyl acrylate, copolymerizations show a linear increase in M_n versus conversion, indicating no transfer during polymerization. Measured molecular weights were consistently higher than theoretical ones, but it was not possible to obtain "universal" molecular weights for our copolymers. Therefore, we presume that the disagreement between measured and theoretical molecular weights is due to comparing copolymers with linear homopolystyrene. Polydispersities in these reaction decrease with increasing conversion to around 1.1, consistent with polydispersities being controlled by an exchange process faster than propagation.

Composition Dependencies and Reactivity Ratios A central question about controlled radical polymerizations catalyzed by transition metal complexes is whether or not the metal center coordinates to the radical. Stereoselectivity and chemoselectivity are

two reaction characteristics which address this question, since a coordinating metal may induce changes in these two quantities, giving polymers differing from their conventional free-radical counterparts. We investigated the chemoselectivity of copolymerizations of styrene and *n*-butyl acrylate by both simulation of experiments and by calculating reactivity ratios from experimental composition data.

Figure 2 shows the predicted and measured styrene cumulative copolymer composition ($F_{cum, styrene}$) versus conversion for nine of the twelve different simultaneous copolymerizations listed in Table 1. The predicted values correspond to the integrated solution of the terminal model composition equation. Experimental errors in composition were estimated by 10 replicate injections of several samples from copolymerizations with different initial conditions, followed by standard error propagation analysis.

Table 1. Reaction Conditions For Statistical Copolymerizations of Styrene and *n*-Butyl Acrylate at 110 °C.

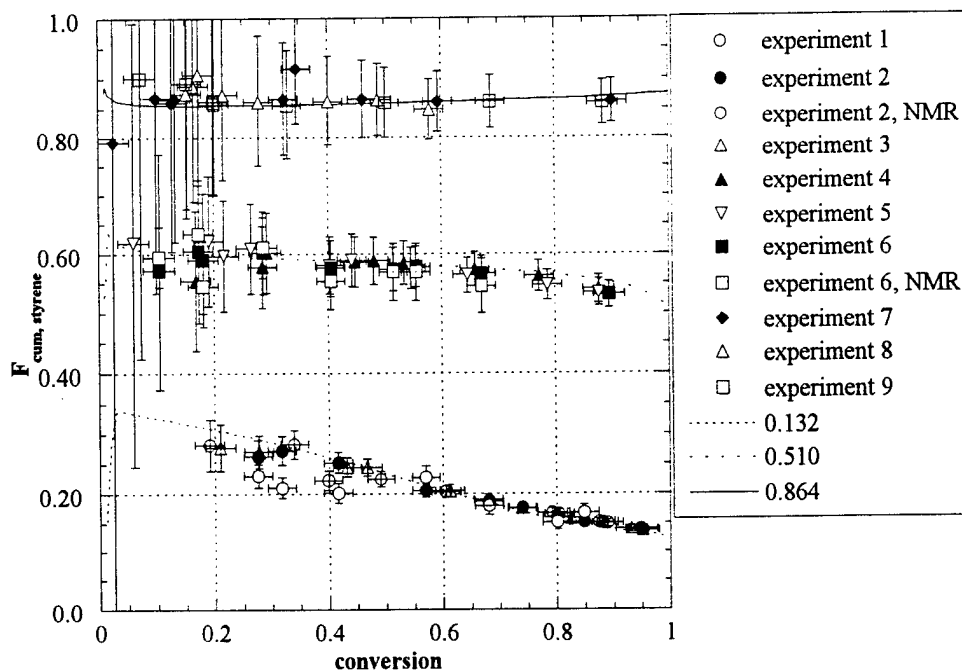| experiment	$(f_{st})_o$	$[M]_o$:$[I]_o$:$[CuBr]_o$:$[dNbpy]_o$
1	0.132	100:1.0:1.0:2.0
2	0.132	101:1.0:1.0:2.0
3	0.132	100:1.0:1.0:2.0
4	0.510	100:1.0:1.0:2.0
5	0.510	100:1.0:1.0:2.0
6	0.510	99:1.0:1.0:2.0
7	0.864	100:1.0:0.9:1.8
8	0.864	101:1.0:0.9:1.8
9	0.864	101:1.0:1.0:2.0
10	0.258	101:1.0:1.0:2.1
11	0.741	102:1.0:1.1:2.2

Figure 2. $F_{cum, styrene}$ versus conversion for simultaneous copolymerizations of styrene and *n*-butyl acrylate at 110 °C. Reaction numbers listed in the legend correspond to conditions in Table 1. Lines indicate the theoretical dependencies simulated with reactivity ratios $r_1 = 0.698$ and $r_2 = 0.164$ Each number for the theoretical line corresponds to the initial styrene feed (($f_{st})_o$) in the simulation.

Figure 2 shows that copolymerizations of styrene and *n*-butyl acrylate by ATRP proceed with the same chemoselectivity as conventional radical polymerizations, indicating that carbon-centered, uncoordinated free radicals are generated during this copolymerization.

Figure 3 shows 95% joint confidence intervals (JCIs) for monomer reactivity ratios evaluated by fitting experimental conversion / composition data to the integrated form of the terminal model composition equation using a non-linear least-squares analysis in conjunction with a "sum-of-squares space visualization" approach.[5,6] Table 2

compares   other   reported   values
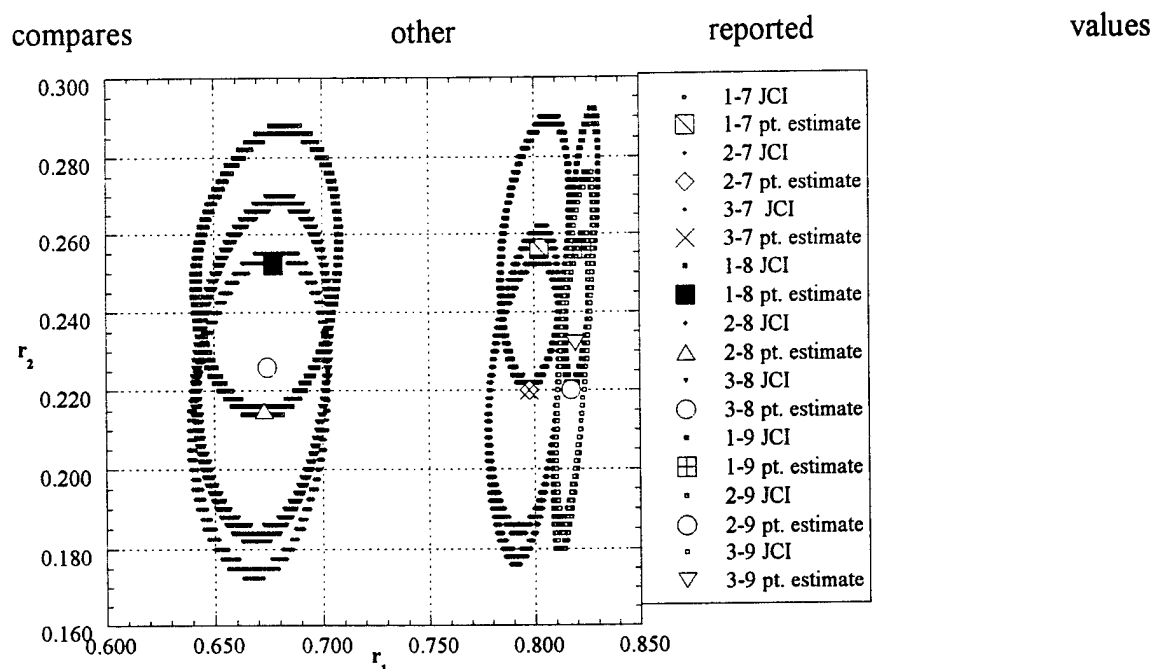

Figure 3. 95% Joint confidence intervals constructed from the SS-space calculations for nine different experimental data set combinations derived from combining $(f_{st})_o$ = 0.132 and $(f_{st})_o$ = 0.864 experiments in Table 2 (experiments 1-3 and 7-9). Each reactivity ratio estimate corresponds to combining one low styrene and one high styrene data set. The numbers in the legend correspond to the experiments combined together, the conditions for which are listed in Table 2. "Pt. estimate" indicates the reactivity ratio point estimate derived from the calculations.

Table 2. Monomer Reactivity Ratios of Styrene (r_1) and n-Butyl Acrylate (r_2) from Various Sources.

method	r_1	r_2	temperature ($\square$C)	reference
Kelen-Tüdös[a]	0.698 ± 0.033	0.164 ± 0.017	50	{Kaszás, 1984 #22}
EVM[a]	1.21 ± 0.21	0.17 ± 0.07	70	{Brar, 1992 #23}
EVM	0.955	0.183	50	{Dube, 1991 #24}
Kelen-Tüdös[a]	0.883	0.207	80	{Ziaee, 1998 #25}
Mayo-Huglin[b]	1.006	0.232	80	{Ziaee, 1998 #25}
SS-space[c,d]	$0.68 \square r_1 \square 0.82$	$0.22 \square r_2 \square 0.26$	110	this work

[a] below 15 % monomer conversion.

[b] above 15 % monomer conversion.

[c] 25 % to 85 % monomer conversion.

of reactivity ratios for this monomer pair with the reactivity ratios we calculated. Our values agree quite well with others, strongly indicating that the chemoselectivites of radicals in copolymerization of styrene and *n*-butyl acrylate by ATRP are very similar to conventional free radical polymerizations. Based on these reactivity ratio values, it was observed that the Sty/BA monomer pair tended to formed random/statistical copolymers, rather than the desired gradient materials. In the preparation of gradient copolymers in a one pot process, it is desirable to copolymerize monomer pairs with very different reactivity ratios to insure a continuous gradient within the formed polymer chain. While gradient copolymers of Sty/BA could be formed by strict control of the monomer feed ratios, we sought to prepare these materials in a convenient one-step procedure. For this reason, other monomer pairs meeting the above specified criteria were explored.

Gradient Copolymers. The synthesis of gradient copolymers from methyl methacrylate (MMA) and *n*-butyl acrylate (BA) by ATRP was conducted. Our focus in this study was to select a monomer pair that would form linear spontaneous gradient copolymers as a model to optimize reaction conditions for the preparation of star and branched gradient copolymers. For this reason, a monomer pair of methyl methacrylate (MMA) and *n*-butyl acrylate (BA) was copolymerized by ATRP, as many of the advantageous physical properties of the copolymer, as seen in the p(Sty/BA) system, are retained while allowing the reaction to be done in a one-pot process.

The ATRP of MMA/BA using the Cu(I)Br/N, N, N', N", N"-pentamethyldiethylenetriamine (PMDETA) catalyst was investigated. The use of the PMDETA ligand for ATRP has been successful for the controlled polymerization of a wide range of monomers. The commercial availability and low cost of the ligand was an additional motivation behind application to copolymerizations of MMA/BA.

Reactivity ratios for the ATRP of MMA and BA using the Cu(I)Br/PMDETA in acetone solutions were calculated ($r_{mma} = 3$ and $r_{ba} = 0.3$) and agreed well with literature values. In the determination of the reactivity ratios, different data sets with varying initial monomer feeds were assayed to ascertain which statistical approach would yield smaller JCI's. In the initial calculation using only a $(f_{ba})_o = 0.5$ data set (black triangles Figure 4),

the largest JCI for the reactivity ratios was obtained. However, by using data sets with both low and high *n*-butyl acrylate feeds, a much lower JCI for the calculation was achieved. The reactivity ratios for the ATRP of MMA/BA using the Cu(I)Br/PMDETA in an acetone solution were found to possess smaller JCI's, but also slightly shifted values (r_{mma} = 3.1, r_{ba} = 0.21). This confirmation of the large difference in reactivity ratios between MMA and BA provided evidence via kinetic data that gradient copolymers were able to be prepared by ATRP.
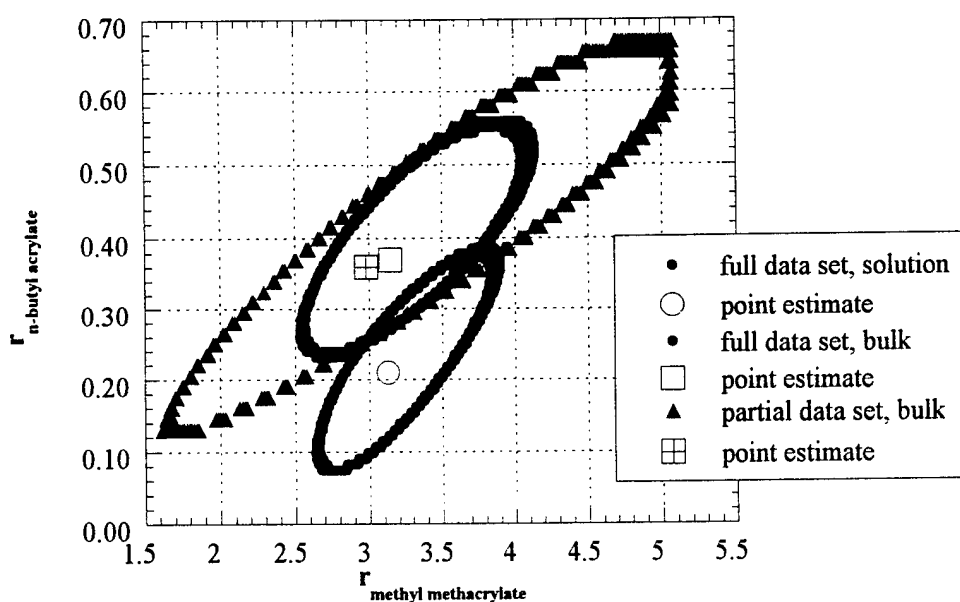

Figure 4. Reactivity ratio calculations for bulk and solution ATRP of MMA/BA using various data sets.

Functionalization of Hyperbranched Polymers. The synthesis of a hyperbranched polyacrylate with terminal epoxide groups at each branch was conducted. Previously, we reported the synthesis of hyperbranched polyacrylates by the self-condensing vinyl polymerization (SCVP)[7] using ATRP.[3,8] Inherent to polymers prepared from ATRP is the presence of activated α-haloesters or benzylic halides at each terminal group of the polymer. While this functionality is useful for chain extension reactions to grow block or other copolymers, the alkyl halide end-group functionality is of limited utility for other chemistries. In addition to the synthesis of hyperbranched p(BIEA), the transformation of alkyl halide end-groups to epoxy functionalities was conducted for hyperbranched p(BPEA). Thus, the incorporation of a reactive functionality, i.e., epoxide, was pursued

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to prepare a functional hyperbranched polymer. The approach that was conducted was the use of atom transfer radical addition (ATRA) chemistry where polymeric alkyl halides prepared from ATRP were functionalized using various alkenes. In our system, the transformation of alkyl halide groups from poly(2-(2-bromopropionyloxy)ethyl acrylate (p(BPEA)) to epoxide groups was done. In this reaction, Cu(I) complexes are employed to abstract halogens from polymeric alkyl halide macroinitiators to generate radicals and Cu(II) deactivating species. Subsequent addition across the double occurs, followed by deactivation of the formed radical with halogen from the Cu(II) species. The synthetic route for the preparation of epoxy-functional hyperbranched p(BPEA) is presented in Scheme 2.

Hyperbranched Poly(BPEA)

1,2-epoxy,5-hexene

Cu(I)Br/dTbpy

Epoxy-Functional p(BPEA)
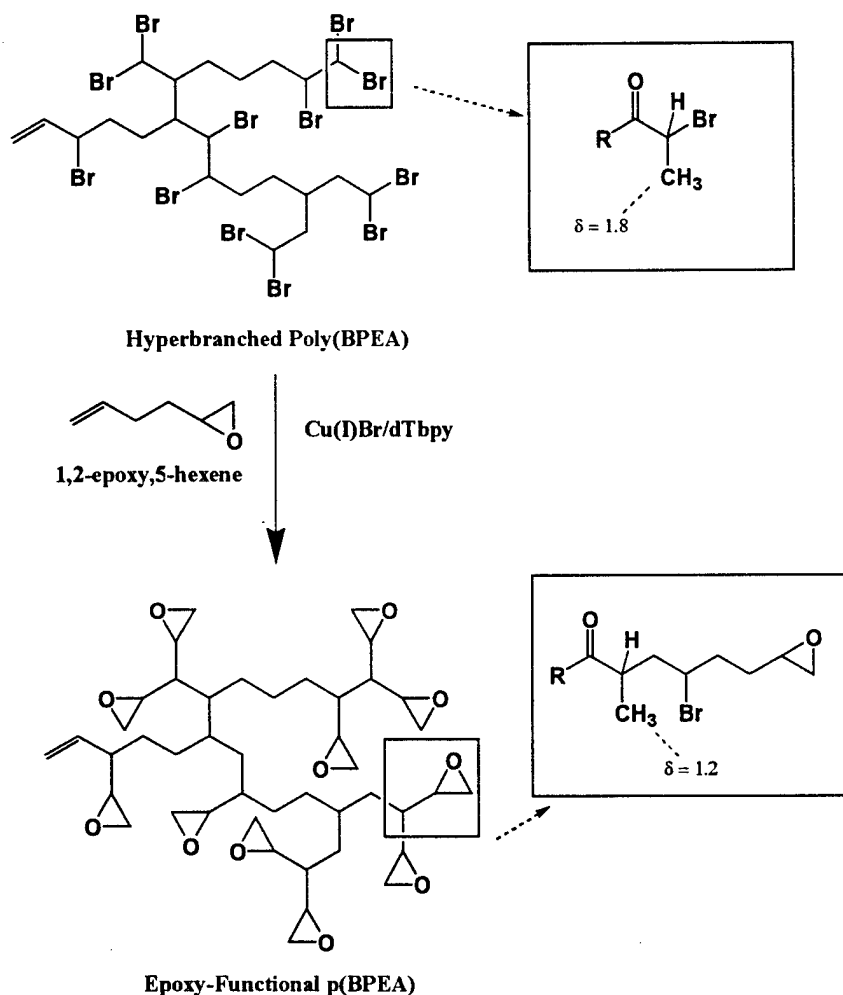
Scheme 2: Functionalization of Hyperbranched Polymers using pBPEA and 1,2-epoxy,5-hexene. [Alkene]:[Cu(I)]:[Ligand] was 155:1:3

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In the ATRA reaction of p(BPEA) and 1,2-epoxy, 5-hexene a Cu(I)Br/(4,4'-di-*t*-butyl, 2,2'-byridine)(dTbpy) homogeneous catalyst system was employed at 70°C. The reaction was able to done in bulk due to solubility of polymer and catalyst in the alkene. A 4:1 wt-ratio of alkene to polymer was used to insure that p(BPEA) did not undergo coupling reactions after generation of radicals. After an appropriate reaction time (~ 8 hrs), the functionalized polymer was recovered by precipitation into hexane.

From ^{1}H NMR analysis, it was observed that conversion of the polymeric alkyl halide (p(BPEA)) to epoxide groups was successful. In the ATRA reaction, resonances at δ = 2.8, 2.5 and 2.2 were observed, indicative of epoxide incorporation, also, as expected, resonances for the end-group moiety of p(BPEA) at δ = 1.8 were no longer observable. The ^{1}H NMR spectra for the reaction is presented below.
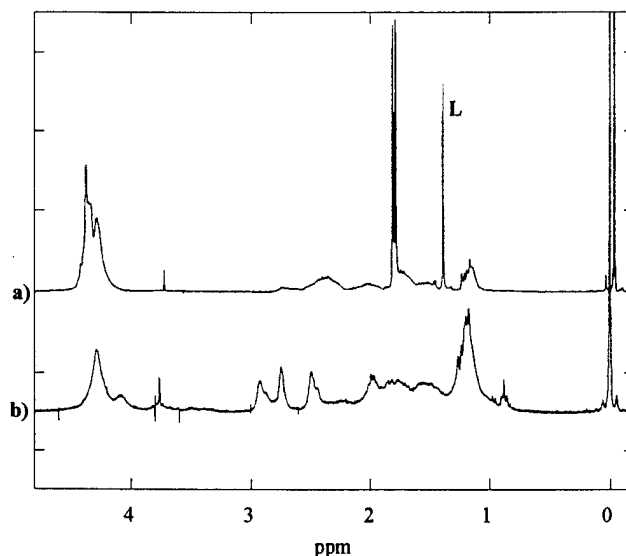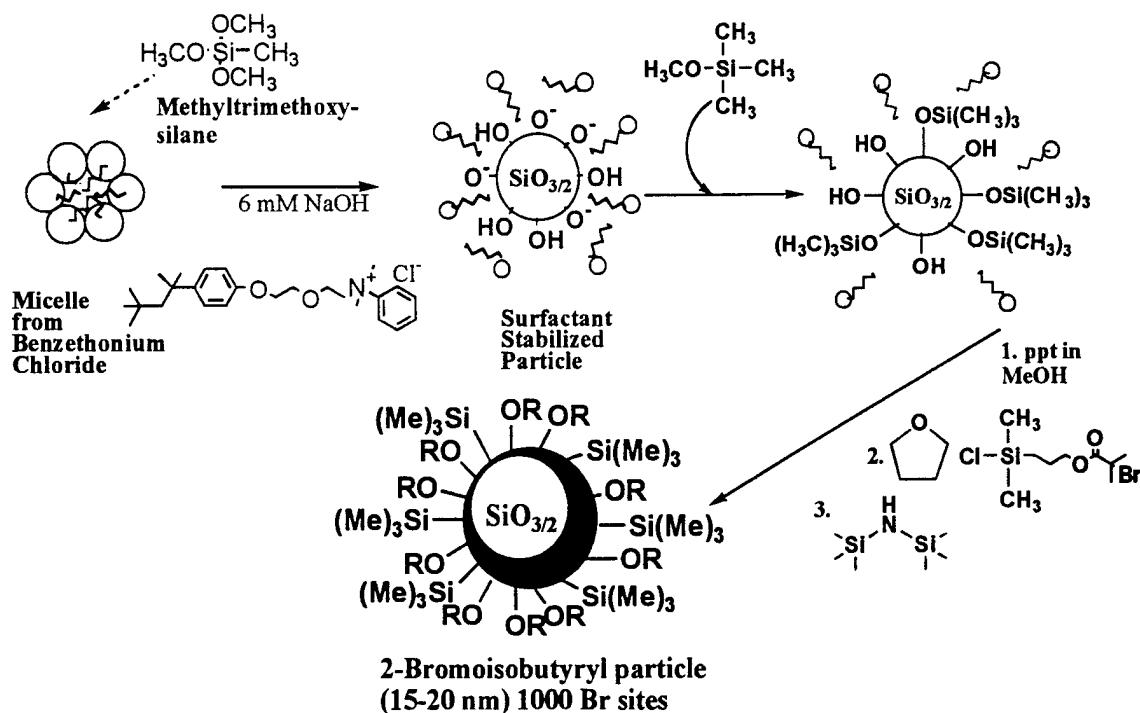

Figure 5: ^{1}H NMR of the hyperbranched p(BPEA), before (a) and after (b) addition of 1,2-epoxy-5-hexene (L = residual ligand)

Multifunctional Initiators toward the preparation of multi-armed gradient star copolymers. Having developed the methodology for the synthesis of linear copolymers,

the preparation of more sophisticated branched structures was pursued. One approach toward the synthesis of highly branched gradient copolymers is the copolymerization of a vinyl monomer (e.g., MMA) with an AB* monomer (e.g., (2-bromopropionyloxy)ethyl acrylate), as previously dicussed. However, due to the high polydispersity and architectural heterogeneity of polymers obtained from self-condensing vinyl polymerization (SCVP) by ATRP, the synthesis of multi-armed star gradient copolymers was proposed. In particular, the ATRP of MMA/BA conducted from multifunctional initiator compounds would enable the preparation of a star polymer with gradient copolymer arms. The primary advantage of using a multifunctional species is that similar reaction conditions as those studied in the ATRP of monomer pairs, such as MMA/BA, can be applied negating the need to use the SCVP process. While multifunctional initiators (functionality = 3,4,6) have been synthesized and applied to the preparation of star- and star block (co)polymers,[9] the synthesis and application to ATRP of initiators possessing degrees of functionality comparable to dendritic polymers have not been extensively investigated.

Toward this endeavor, the synthesis of silicate nanoparticles, possessing ATRP initiator groups, was pursued. The capability to incorporate a large number of initiating sites to the particle (700-10,000), star polymers with a high density of gradient copolymer arms can be prepared. Such a material is anticipated to possess many of the advantageous properties of dendritic polymers (i.e., low viscosity, high functionality). Additionally, the copolymer arms can be cleaved by acidic hydrolysis of the silicate core with hydrofluoric acid (HF) and then characterized to ascertain the molecular weight and composition of the copolymer chain. The general route for the synthesis of functional silicate particles and highly branched nanocomposites from ATRP is presented in Schemes 3 and 4.

Scheme 3 Diagram

Starting material (top left):

OCH₃
H₃CO·Si—CH₃
  OCH₃

Methyltrimethoxy-silane

6 mM NaOH →

Micelle from Benzethonium Chloride

Surfactant Stabilized Particle (SiO₃/₂ with HO, O⁻, OH groups)

CH₃
H₃CO-Si-CH₃
  CH₃
→

Surface-modified particle: SiO₃/₂ with OSi(CH₃)₃, OH, HO, (H₃C)₃SiO groups

1. ppt in MeOH

2. Cl-Si(CH₃)₂~O~O~Br

3. Si-N(H)-Si (disilazane)

2-Bromoisobutyryl particle
(15-20 nm) 1000 Br sites

(SiO₃/₂ core with (Me)₃Si, RO, Si(Me)₃, OR groups)

Scheme 3: Synthesis of Functional Colloids For ATRP

The synthesis of functional nanoparticles and nanocomposites is being done in collaboration with Prof. Manfred Schmidt of the Univ. of Mainz. Previous work by Schmidt et al,[10] reported the preparation of monodisperse, highly, functional silicate nanoparticle, with particle sizes in the order of 10 nm ($M_w \sim 2 \times 10^6$). In this system, surfactant (benzethonium chloride) forms micelles, which serve as nanosize templates and reactors for the preparation of particles. This process is the analogous to microemulsion polymerizations for polymeric latex particles. Surfactant then stabilizes the surface of the particle, allowing for consecutive condensation reactions on the surface of the preformed particle with other silanes. In this way, various functionalities can be introduced to the surface of the particle. Particle sizes can be tuned by varying concentration of surfactant relative to silane in the range of 10-30 nm. Another feature of this system is that soluble particles can be prepared by deactivation of surface silanol groups with monoalkoxysilanes and disilazanes (Scheme 3). The deactivation of surface silanol groups on particles is vital toward the preparation of particles that are soluble in conventional nonpolar organic solvents. Incomplete surface deactivation may result in irreversible aggregation between particles from condensation of surface silanol groups. As shown in Scheme 3, monoalkoxysilanes are condensed on particle surfaces in aqueous

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media, in the presence of surfactant. While this step does not completely react with surface silanol groups, particles are sufficiently coated to enable precipitation into poor solvents (e.g., methanol) without irreversible aggregation. To achieve complete deactivation of silanol surface groups further treatment with either disilazanes, or monochlorosilanes in organic media is required. The direct treatment of particles with disilazanes/monochlorosilanes in surfactant-stabilized aqueous media cannot be done due to the hygroscopic nature of the reagents.

Characterization of the 2-bromoisobutyryl functional colloids was conducted by dynamic light scattering (DLS), atomic force microscopy (AFM) and elemental analysis. From DLS, the diameters of the colloids were found to be 15-20 nm, possessing a low polydispersity of particle sizes. This result was confirmed by AFM, where using bearing analysis, the particle sizes were found to be 16 nm. Elemental analysis confirmed the incorporation of ATRP initiating sites to the nanoparticle (4-wt% Br), and it was calculated that approximately 1000 initiating sites were present per particle.
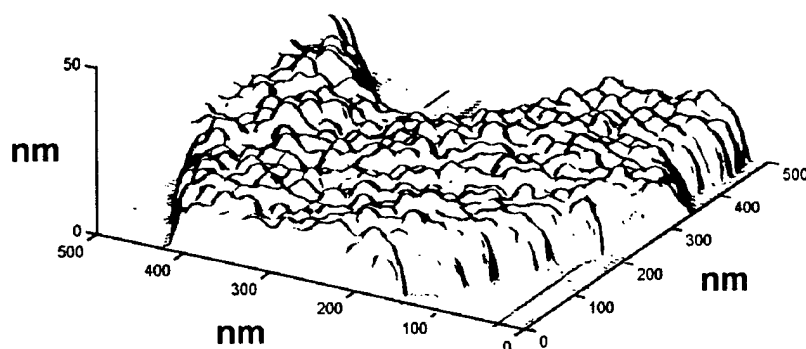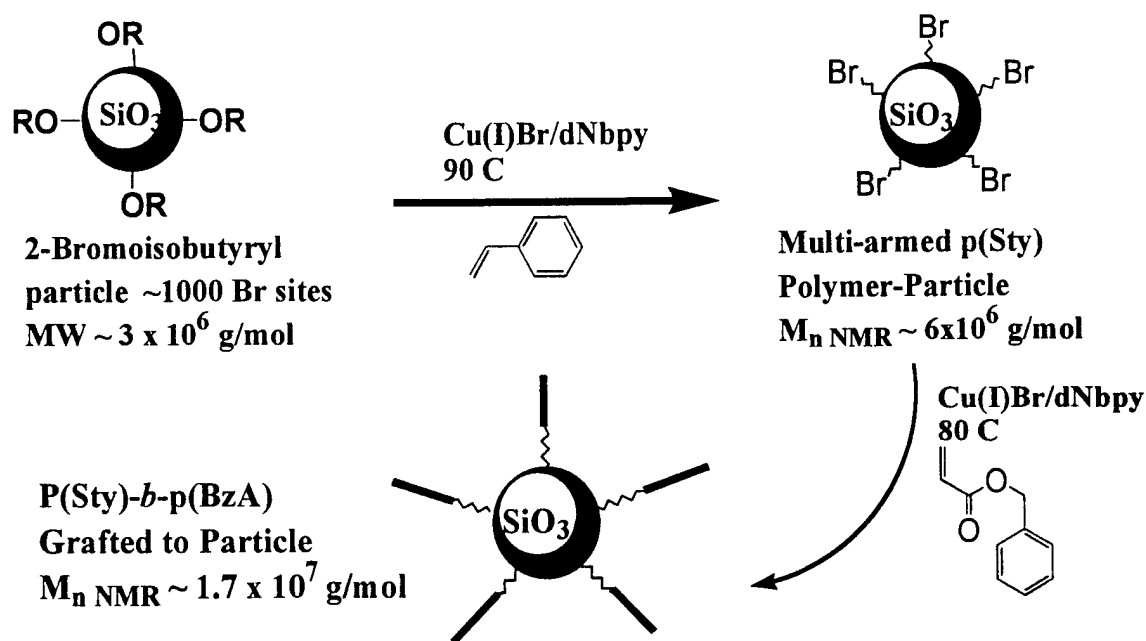

Figure 6: AFM image of 2-Bromoisobutyryl Functional Nanoparticles

The synthesis of polymer-particle nanocomposites was then performed by the ATRP of vinyl monomers using the functional colloids as initiators. From this approach, hybrid particles with homopolymers of poly(styrene) (p(Sty) and block copolymers of poly(styrene)-*b*-poly(benzyl acrylate) (p(Sty)-*b*-p(BzA)) tethered to nanoparticles were prepared. To our knowledge, this is the first report on the synthesis of block copolymers tethered to colloid surfaces. The synthetic scheme and conditions for the ATRP reactions are presented in Scheme 4.

OR

RO—SiO₃—OR

OR

2-Bromoisobutyryl
particle ~1000 Br sites
$MW \sim 3 \times 10^6$ g/mol

Cu(I)Br/dNbpy
90 C

Br
Br—SiO₃—Br
Br   Br

Multi-armed p(Sty)
Polymer-Particle
$M_{n\,NMR} \sim 6 \times 10^6$ g/mol

Cu(I)Br/dNbpy
80 C

P(Sty)-*b*-p(BzA)
Grafted to Particle
$M_{n\,NMR} \sim 1.7 \times 10^7$ g/mol

Scheme 4: Synthesis of Block copolymers tethered to Nanoparticles

It has been demonstrated that films of polymer-particle hybrids result in hexagonally packed arrays of nanoparticles with a periodicity dependent on the molar mass of the tethered polymers.[11] AFM analysis of our hybrid particles confirmed that block copolymers were grafted to the particle surfaces and that effective diameter of the particle increased from 15 nm (bare particle) to 55 nm (block copolymer particle) (Figure 7). Additionally, films of these block copolymer hybrid particles yielded periodic arrays of nanoparticles. As seen in the AFM images, particles are shown as dark spots embedded in a lighter colored polymer matrix which is tethered copolymers of p(Sty)-*b*-p(BzA). From this work, we demonstrate the ability to modify the property of colloidal materials by polymerizing functional monomers in a controlled manner by ATRP. We anticipate these nanocomposite materials will have great potential as nanofillers, blend compatibilizers and supported catalysts.
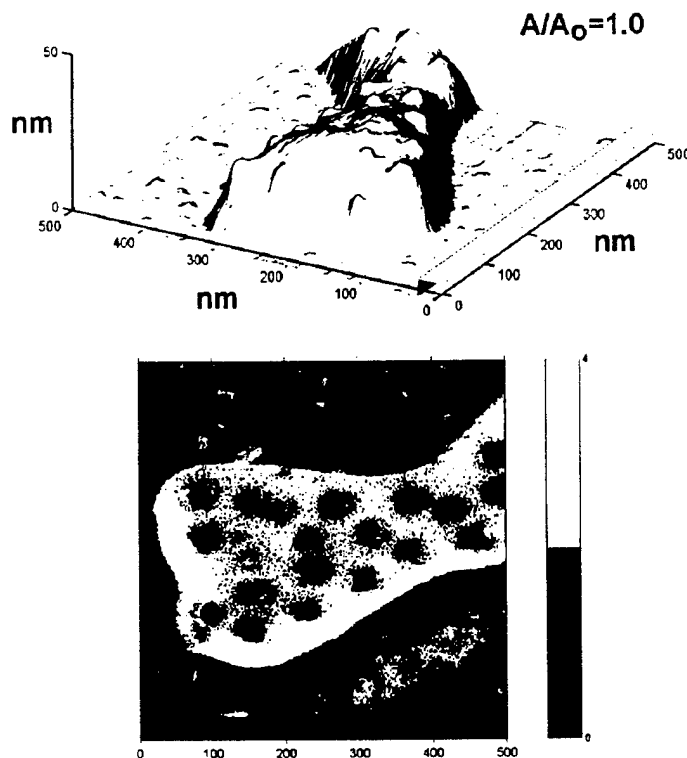
Figure 7: AFM Image of p(Sty)-*b*-p(BzA) bound to Silicate Nanoparticle
Surface area/particle = 3020 nm^2; D$_{eff}$ = 55 nm

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Technology Transfer

a. *Have you given or are you preparing to give samples, data, or a process to the Army for evaluation or use?*

Samples from this research have not been given to the Army for evaluation.

b. *Any patents filed or approved?*

No patents based on the previously described research has been filed.

c. *List the names and organization of all those in the Government to whom you send your reports and publications. "d" below is related to this, but goes beyond simply sending reports or papers.*

We have not sent reports to other government agencies.

d. *Have there been any interactions with the Army, DoD, or industry, such as research results transfer, research discussions, or personal meetings, that go simply beyond sending them reports and papers as listed in "c" above?*

There has not been any such interactions.

e. *Were there any breakthroughs such as developing a new instrument, technique, or process that may significantly impact you own, or other's research in industry?*

Our work in the synthesis of highly functional branched polymers is of interest due to the incorporation of reactive groups, to a highly functional, low viscosity polymer. Such a material is can be prepared in a one pot process and may be useful in fields such as resin and coating technologies. Additionally, the preparation of nanocomposites with organic shells and inorganic cores represents a new class of materials with unexplored properties and potential applications.

f. *Do you have any interesting samples or other physical items (including pictures) I could use to demonstrate some aspect of your research, or results?*

We do not such tangibles at this time.

g. *Are there interactions with other ARO Pi's? E-mail/phone interactions are noteworthy, as are face-to-face meetings and, of course, research collaborations.*

We have had no interactions with other ARO associates.

h. *Have any of you students gone to work permanently, or temporarily for or with the Army or DoD during the current grant, or traveled to an Army lab to work with the Army as part of the current grant?*

None of our students have gone to work with the Army, or DoD.

i. *Has anyone (not counting Programs related to me such as DURIP and AASERT) given you manpower, supplies, samples, equipment, information, or research funds that are leveraged in any way for the ARO effort?*

Krzysztof Matyjaszewski participated in the workshop on novel materials hosted by the Air Force in August 1999

List of scientific personnel supported and honors and awards received.

Krzysztof Matyjaszewski has received the following awards:

A. von Humboldt prize for Senior U.S. Scientist (1999)